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(54) INK, AND METHOD AND APPARATUS FOR INK JET RECORDING USING THE SAME

(57)Abstract:

PURPOSE: To obtain an ink which can be applied to any desired recording material, gives a weather-resistant record with a good print quality, and is suitable for ink jet recording by using a water-sol. resin and a water-sol. monomer as the essential components.

CONSTITUTION: An ink is prepd. by dispersing or dissolving a pigment, a water-sol. resin pref. having a wt.-average mol.wt. of 3,000-30,000, a water-sol. monomer which solidifies when it receives energy (e.g. an ultraviolet-polymerizable monomer, pref. an acrylic or epoxy monomer), and a photopolymn. initiator in an aq. medium. A dye may be jointly used with the pigment, pref. in a wt. ratio of (8:2)-(2:8). The ink is applied to a recording medium by ink jet method and cured by exposing to ultraviolet rays, heat, or an electron beam.

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CLAIMS

[Claim(s)]

[Claim 1] an aqueous solvent — the ink characterized by including a pigment, water soluble resin, the water-soluble monomer solidified by grant of energy, and a photopolymerization initiator at least inside of the body.

[Claim 2] Ink according to claim 1 which has the weight average molecular weight of said water soluble resin in the range of 3000 thru/or 30000.

[Claim 3] Ink according to claim 1 which has said pigment in a distributed condition.

[Claim 4] Furthermore, ink containing a color according to claim 1.

[Claim 5] Ink according to claim 4 which has said pigment and said color in the range of 8:2-2:8 by the weight ratio.

[Claim 6] Ink according to claim 1 which contains the monomer which has a polyfunctional radical as said water-soluble monomer.

[Claim 7] Ink according to claim 1 which contains said water-soluble monomer in 1% - 10% of range of all ink weight.

[Claim 8] Ink according to claim 1 said whose energy is ultraviolet rays, heat, or an electron ray.

[Claim 9] Ink according to claim 1 which adjusted viscosity to 10cps or less.

[Claim 10] Ink according to claim 1 which adjusted pH to the range of 7-10.

[Claim 11] Ink containing 50% or more of water of all ink weight according to claim 1.

[Claim 12] The ink jet record approach characterized by applying the ink of a publication to said claim 1 thru/or any 1 of 11 as said ink in the ink jet record approach which records by making the ink droplet formed with the ink jet method adhere to a recorded material.

[Claim 13] The ink jet record approach according to claim 12 that said ink jet method is a method which makes heat energy act on ink.

[Claim 14] The ink jet record approach according to claim 12 that said recorded material is a thing without ink absorptivity.

[Claim 15] Furthermore, the ink jet record approach according to claim 12 of having the process which gives ultraviolet rays, heat, or an electron ray to the ink adhering to a recorded material.

[Claim 16] The ink cartridge characterized by applying the ink of a publication to said claim 1 thru/or any 1 of 11 as said ink in the ink cartridge which has the ink hold section which held ink.

[Claim 17] The record unit characterized by applying the ink of a publication to said claim 1 thru/or any 1 of 11 as said ink in the record unit which has both the head sections to carry out the regurgitation, using as an ink droplet the ink hold section which held ink, and said ink.

[Claim 18] The record unit according to claim 17 which heat energy is made to act on said ink, and performs the ink regurgitation in said head section.

[Claim 19] The ink jet recording apparatus characterized by having an ink cartridge or a record unit given in any [said claim 16 thru/or] of 18 they are in the ink jet recording apparatus which records by making the ink droplet formed with the ink jet method adhere to a recorded material.

[Claim 20] The ink jet recording device according to claim 19 further equipped with a means to irradiate ultraviolet rays, heat, or an electron ray, to said recorded material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the ink jet record approach using this ink, and the equipment for ink jets which applied this ink further about ink and the ink which suits record to the medium which does not especially have ink absorptivity.

[0002]

[Description of the Prior Art] There is solid ink which dissolves a color in the drainage system ink which dissolved the color in the drainage system solvent as a color material, and the wax system solvent solidified in ordinary temperature as ink of the ink jet recording device printed by injecting liquid ink from a head nozzle, and is injected and printed from a head where heating fusion is carried out.

[0003] Moreover, about the ink for an ink jet print of an ultraviolet curing mold, there are some which used water soluble dye as indicated by JP 5-186725A, and printing to a regular paper and recycled paper is made easy.

[0004] Moreover, to the plastic plate, as the image formation approach, the sublimability color is used for ultraviolet curing mold resin as indicated by JP,52-142516.A.

[0005]

[Problem(s) to be Solved by the Invention] There is a problem shown below in a Prior art.

[0006] When using 1 and drainage system ink for color printing (for example, when it printed by the first amorous glance, and the second amorous glance is printed after the first amorous glance dried) and the dot of the second amorous glance lapped with the first amorous glance, there was a problem on which the color of the first amorous glance remelts and bleeds and printing grace gets worse.

[0007] Since they use the solvent permeability to paper, if plastics is used as recorded materials, while 2 and drainage system ink will require time amount by ink desiccation, they cannot form an image with abrasion resistance. Therefore, as a recorded material, paper will be applicable.

[0008] Although a color does not bleed even if moisture adheres to 3 and ultraviolet curing mold resin again after printing in the ink which mixed water soluble dye, the color by UV irradiation fading is not avoided.

[0009] Although a recorded material is not chosen in 4 and solid ink, since it is the soft quality of the material of a wax, a printing dot will peel easily also in weak frictional force. Moreover, since the ink which generally contains an organic solvent makes a solvent smell emit, there is [a problem] to an environment.

[0101] It is necessary to heat a recorded material at 120–180 degrees C about the ink which used the sublimability color for 5 and ultraviolet-rays hardening resin, and a recorded material is restricted.

[0011]

[Means for Solving the Problem] Then, the purpose of this invention does not choose a recorded material, but is to offer the ink jet record approach and recording device using the ink which enables good record of printing grace with weatherability, and this.

[0012] The above-mentioned purpose is attained by the following this inventions.

[0013] That is, it is the ink jet record approach characterized by for this invention being a pigment, water soluble resin, the water-soluble monomer solidified by graft of energy, and ink characterized by including a photopolymerization initiator at least, and this invention applying the ink of said this invention as said ink into an aqueous liquid solvent in the ink jet record approach which records the ink droplet formed with the ink jet method by making it adhere to a recorded material.

[0014] Furthermore, this invention is an ink cartridge characterized by to apply the ink of said this invention as said ink in the ink cartridge which has the ink hold section which held ink, and is a record unit characterized by to apply the ink of said this invention as said ink in the record unit which has both the head sections to carry out the regurgitation, using as an ink droplet the ink hold section which held ink, and said ink.

[0015] In addition, another this invention is an ink jet recording apparatus characterized by having an aforementioned ink cartridge or an aforementioned record unit in the ink jet recording apparatus which records by making the ink droplet formed with the ink jet method adhere to a recorded material.

[0016]

[The desirable mode of this invention] It explains per desirable mode of this invention below.

[0017] An ultraviolet-rays polymerization monomer is mentioned as a monomer solidified by grant of energy in this invention, and the acrylic monomers of radical polymerization nature and the epoxy monomers which suit a cationic polymerization system can use it suitably.

[0018] As acrylic monomers of radical polymerization nature N and N-dimethylaminoethyl methacrylate, CH₂=C(CH₃)-COO-CH₂CH₂N₂(CH₃): N and N-dimethylamino ethyl acrylate, CH₂=CH-COO-CH₂CH₂N₂(CH₃): N and N-dimethylaminopropyl methacrylate, CH₂=C(CH₃)-COO-CH₂CH₂CH₂N₂(CH₃): N and N-dimethylaminopropylacrylate, CH₂

=CH-COO-CH₂ CH₂ CH₂ N₂ (CH₃) : N and N-dimethylamino acrylamide, CH₂ =CH-CON(CH₃)₂ N and N-dimethylamino meta-acrylamide, CH₂ =C(CH₃)-CON₂ (CH₃) : N and N-dimethylaminoethyl acrylamide, CH₂ =CH-CONHC₂H₄ N₂ (CH₃) : N and N-dimethylaminoethyl meta-acrylamide, CH₂ =C(CH₃)-CONHC₂H₄ N₂ (CH₃) : N,N-dimethylaminopropyl acrylamide, CH₂ =CH-CONH-C₃H₆ N₂ (CH₃) : N and N-dimethylaminopropyl meta-acrylamide, CH₂ =C(CH₃)-CONH-C₃H₆ N₂ (CH₃) : And these matter formed into 4 class is especially excellent in color-material dyeing property, and desirable. Moreover, ultraviolet curing mold monomers well-known in itself, such as a reactant of the acrylic ester (meta) of polyhydric alcohol, the acrylic ester (meta) of the glycidyl ether of polyhydric alcohol, the acrylic ester (meta) of a polyethylene glycol, the acrylic ester (meta) of the ethylene oxide addition compound of polyhydric alcohol, and a polybasic acid anhydride and hydroxyl-group content (meta) acrylic ester, and oligomer are used. In these matter, the high matter of compatibility with ink and a hydrophilic property is chosen, and it is used.

[0019] As epoxy monomers which suit a cationic polymerization system, the glycidyl ether of polyhydric alcohol, glycidyl ester, aliphatic series annular epoxide, etc. are used.

[0020] In this invention, in order to use a pigment as a color material, the cure rate of a monomer tends to become slow. Therefore, as a polymerization system of the monomer of UV polymerization, the monomer of the high Brit polymerization system which is using vinyl ether and acryloyls together is desirable, and, subsequently to the order of a cationic polymerization system and a free radical polymerization system, selects. When using the monomer which has a polyfunctional radical, the amount used has 1 - 10% of desirable range to all ink weight.

[0021] As a usage of a photopolymerization initiator, one-kind use, two or more kind use, a photoinitiator, and a sensitizer may be used for a photoinitiator. What is necessary is to select suitably and just to go about selection of the main photoinitiators and sensitizers, combination, and a compounding ratio, with the ultraviolet curing monomer and the equipment used to be used.

[0022] As main things of a photoinitiator and a sensitizer, it is related with a photoinitiator. Acetophenone, 2, and 2-diethoxy acetophenone, p-dimethylamino aceto FEN, p-dimethylamino propiophenone, a benzophenone, 2-chlorobenzo phenon, pp'-dichloro benzo FEN, a pp'-bis-diethylamino benzophenone, A Michler's ketone, benzyl, a benzoin, benzoin methyl ether, Benzoin ethyl ether, benzoin iso-propyl ether, the benzoin n-propyl ether, Benzoin isobutyl ether, benzoin n-butyl ether, benzyl dimethyl ketal, Tetramethylthiuram monosulfide, thioxanthone, 2-chloro thioxanthone, 2-methylthioxanthone, azobisisobutyronitril, benzoin peroxide, G tert-butyl peroxide, 1-hydroxy cyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenyl-1-ON, 1-(4-isopropyl phenyl)-2-hydroxy-isobutane-1-ON, and methyl benzoyl FO mate ** are mentioned. The amount used is usually 0.1 - 10 % of the weight to the total amount of ultraviolet-rays hardenability resin. Moreover, in a cationic polymerization mold, photoinitiators, such as aromatic series diazonium salt, an aromatic series halo NIUMU salt, aromatic series sulfonium salt, and a metallocene compound, are used. Triphenyl SURUFONYUUMU hexafluoro phosphate, diphenyl iodine nium hexafluoroantimonate, etc. are mentioned as the example. Moreover, in the case of a cationic polymerization mold, in order to make hardening still more perfect, it is the range of 80-170 degrees C, and it is desirable to heat in 100-150 degrees C desirably especially. Although heating time changes with conditions, it is usually for 5 - 30 minutes.

[0023] The amine which contains 1 amine system:fatty amine and an aromatic series radical as a sensitizer, Piperidine 2 urea : An allyl compound system, o-tolyl thiourea 3 sulfur compound:sodium diethyl dithiophosphate, The fusibility salt 4 nitril system compound of an aromatic series sulfinic acid : N, N, a JI permutation p amino benzonitrile, R1 R1 Methyl group, ethyl group, B cyano ethyl group, or B chloro ethyl group 5 phosphorus compounds : [Tri-n-butyl phosphine,] NETORIUMU diethyl JICHIOHOSU feed 6 nitride : A Michler's ketone, N NITORISO hydroxylamine derivative, an oxazolidine compound, and tetrahydro one — 1 and 3 oxazine compounds — Condensate 7 chlorine compound of formaldehyde or an acetaldehyde, and diamine: A carbon tetrachloride, the macromolecule-sized amine of the resultant of hexachloroethane 8 epoxy resin and an amine, and a triethanolamine thoria chestnut rate are mentioned.

[0024] As a pigment used by this invention, all of organic [well-known] and an inorganic pigment can be used conventionally. For example, inorganic pigments, such as organic pigments, such as color lakes, such as polycyclic type pigments, such as azo pigments, such as an azo lake, insoluble azo pigment, a disazo condensation pigment, and a chelate azo pigment, a phthalocyanine pigment, perylene and a perylene pigment, an ANTOSE quinone pigment, a quinacridone pigment, a dioxazine pigment, a thio ISHIJIGO pigment, an isoindolinone pigment, and a kino FUTARONI pigment, and a basic dye mold lake, an acid-dye mold lake, and a nitro pigment, a nitroso pigment, aniline black, a daylight fluorescent pigment, titanium oxide a ferrous-oxide system, and a carbon black system be mentioned. Moreover, anything can be used, if the distribution to aqueosity is possible even if it is the pigment which is not indicated by the Color Index.

[0025] Furthermore, in this invention, when using a color together, in the technical field concerned, various well-known colors can be used from the former.

[0026] For example, the azo dye as direct dye, phthalocyanine dye, the azo dye as acid dye, an anthraquinone system color, etc. are mentioned.

[0027] In this invention, when using a pigment and a color together, generally it is desirable for the range of a pigment:color (weight ratio) to be 8:2-2:8. It considers as the range of 7:3-3:7 (pigment: color) more preferably.

[0028] The water soluble resin (distributed resin) contained in order to distribute the ink pigment of this invention is meltable in the water solution in which the amine or the base was dissolved, and its weight average molecular weight is [the range of 3000 to 30000] desirable. Furthermore, that whose range is 5000 to 15000 preferably is good. For example, a styrene-acrylic-acid copolymer, a styrene-acrylic-acid-acrylic-acid alkyl ester copolymer, A styrene-maleic-acid copolymer, a styrene-maleic-acid-acrylic-acid alkyl ester copolymer, A styrene-methacrylic-acid copolymer, a styrene-methacrylic-acid-acrylic-acid alkyl ester copolymer, A styrene-maleic-acid half ester copolymer, a vinyl naphthalene-acrylic-acid copolymer, a vinyl naphthalene-maleic-acid copolymer, styrene-maleic-anhydride-maleic-acid half ester copolymers, or these salts can be used.

[0029] As a measuring method of the weight average molecular weight of the above water soluble resin, although various approaches are mentioned, it is common to measure by GPC (gel bar MIESHON chromatography) etc.

[0030] Furthermore, preferably, since that the whole ink is adjusted to neutrality or alkalinity can use the ink of this invention as the ink which raised the solubility of the above mentioned water soluble resin, and was excellent in much more mothball stability, it is desirable. Since pH of ink may cause corrosion of the various members currently used for the ink jet recording device, it is desirable to consider as the range of pH of 7-10 preferably.

[0031] Moreover, as a pH regulator used in the aqueous medium of this invention, inorganic alkali chemicals, such as a hydroxy compound of alkali metal, such as various organic amines, such as diethanolamine and triethanolamine, and a sodium hydroxide, a lithium hydroxide, a potassium hydroxide, an organic acid, and a mineral acid are mentioned, for example.

[0032] Like the above, it carries out, and a pigment and water soluble resin are distributed or dissolved into a water-soluble medium.

[0033] In the ink of this invention, a suitable aqueous medium is the mixed solvent of water and a water-soluble organic solvent, and it is [water] desirable to use not the common water containing various ion but ion exchange water (deionized water).

[0034] As a water-soluble organic solvent used mixing with water For example, methyl alcohol, ethyl alcohol, n-propyl alcohol, Isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, Alkyl alcohols with 1-4 carbonization, such as tert-butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; An acetone, the keto alcohol; tetrahydrofuran of diacetone alcohol, Ether, such as dioxane; Poly ARUKOREN glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, alkylene glycol; in which alkylene groups, such as a diethylene glycol, contain 2-6 carbon atoms — glycerol: — the ethylene glycol monomethyl (or ethyl) ether — The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol methyl (or ethyl) ether and the triethylene glycol monomethyl (or ethyl) ether; a N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, etc. are mentioned.

[0035] Moreover, an organic amine neutralizes a dispersant, and in order to adjust pH of ink to a neutral - basic field, the whole ink makes it contain it 0.001 to 10% of the weight preferably in the ink of this invention in the water-soluble organic solvent of these many.

[0036] Moreover, although it is suitably chosen according to a request and optimum dose contains about the water-soluble above-mentioned organic solvents other than an organic amine, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as a diethylene glycol, and the triethylene glycol monomethyl (or ethyl) ether, is desirable especially.

[0037] Furthermore, in order to acquire the stability of the regurgitation, it found out that it was effective to add aliphatic series monohydric alcohol, for example, ethanol, or isopropyl alcohol 3% or more. That is, it is considered since foaming on the exoergic resistor of the thin film of ink can be carried out more to stability by adding these solvents.

[0038] Furthermore, as effectiveness of these solvents, by adding these solvents to dispersion liquid, generating of the bubble at the time of distribution is suppressed, and it can mention that efficient distribution can be performed.

[0039] Moreover, the ink of this invention can add a surfactant, a defoaming agent, antiseptics, etc. further, in order to consider as the ink which has a desired physical-properties value if needed besides the above-mentioned component. Furthermore, commercial water soluble dye etc. can be added.

[0040] For example, as a surfactant, there are nonionic surfactants, such as anionic surfactants, such as fatty-acid salts, higher-alcohol sulfate salts, liquid fatty-oil sulfate salts, and alkyl allyl compound sulfonates, polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, and polyoxyethylene sorbitan alkyl ester, and these one sort or two sorts or more can be used, choosing them suitably. Although the amount used changes with dispersants, 0.01 - 5 % of the weight is desirable to the ink whole quantity.

[0041] Under the present circumstances, as for the surface tension of ink, it is desirable to determine that the addition of a surfactant will become 30 or more dyne/cm. It is because the situation which is not desirable as for printing **** (gap of the impact area of an ink droplet) at the tip of a nozzle depended for getting wet is caused in a recording method like this invention that a value with the surface tension of ink smaller than this is shown.

[0042] As engine performance generally required of the ink for ink jets, although physical properties, such as viscosity of ink, surface tension, and pH, were mentioned, even if satisfied with a dispersed system like watercolor pigment ink of these physical properties, there were many cases where foaming of ink was unstable.

[0043] Then, it found out not generating a deposit on a thin film resistor, even if it is the thing of all ink weight preferably considered as 1% or less 2% or less about the amount of the water soluble resin which is dissolving into ink as a result of are thermally [this invention persons] stable in watercolor pigment ink and studying wholeheartedly the engine performance of the ink in which the still more nearly optimal foaming is possible, it foams correctly also on the drive conditions of versatility [ink] on a resistor and it continues for a long period of time further. That is, when excessive water soluble resin existed in ink so much to the pigment, even if it gave predetermined heat energy on the thin film resistor, ink did not foam, or the water soluble resin of these surpluses became insoluble matter with the heat at the time of pulse impression, and it deposited on the thin film resistor, and had become the cause which causes turbulence of the non-regurgitation or printing.

[0044] The water soluble resin which is dissolving here points out the resin in the condition of having dissolved into the liquid medium without sticking to a pigment into ink. One means to reduce the amount of this water soluble resin that is dissolving is 3:1-30:1, and adjusting to the range of 10:3-30:1 preferably in a weight ratio about the ratio of a pigment and water soluble resin at ink creation time.

[0045] Furthermore, as for the pigment in dispersion liquid, and the total amount of water soluble resin, it is desirable that it is 30% or less preferably 10% or more on weight criteria. It is because it cannot distribute efficiently and the optimal distributed condition cannot be acquired as the reason, unless the pigment and water soluble resin more than fixed concentration exist in dispersion liquid.

[0046] After adding and stirring a pigment first as the preparation approach of the water-soluble pigment dispersing element of this invention in the water solution which contains water soluble resin (distributed resin), an amine, and water at least, it distributes using the below-mentioned distributed processing, centrifugal separation processing is performed if needed, and desired dispersion liquid are obtained. Next, a component which was mentioned by the above which contains

polymethylmethacrylate in these dispersion liquid is added and stirred, and it considers as ink.

[0047] Here, as ink of this invention, the viscosity is preferably adjusted to 10cps or less.

[0048] In order to especially make the amount of the water soluble resin (resin for which a pigment is not adsorbed) which is dissolving into ink 2% or less, in the creation approach, it is required to stir the water solution containing resin, an amine, and water more than for 60 degrees C and 3 minutes, and to dissolve resin completely beforehand.

[0049] Moreover, it is required for the amine for which it asked by count from the acid number of resin, or the amount of bases to add the amount of the amine in which resin is dissolved, or a base 1.2 or more times. The amount of this amine or a base is calculated by the following formulas.

[0050]

[External Character 1]

$$\text{アミンの量 (g)} = \frac{\text{樹脂の酸価} \times \text{アミンの分子量} \times \text{樹脂量(g)}}{56000}$$

[0051] Furthermore, before carrying out distributed processing of the water solution containing a pigment, it is also required to perform pre mixing more than for 30 minutes. This pre mixing actuation is for improving the wettability on the front face of a pigment, and promoting adsorption on a pigment front face.

[0052] As amines added by part acid liquid, organic amines, such as monoethanolamine, diethanolamine, triethanolamine, aminomethyl propanol, and ammonia, are desirable.

[0053] On the other hand, although what kind of thing may be used as long as the disperser used for this invention is a disperser generally used, a ball mill, a roll mill, a sand mill, etc. are mentioned, for example.

[0054] Also in it, the sand mill of a high-speed mold is desirable, for example, a super mill, a Sand grinder, a bead mill, an agitator mill, a grain mill, a die no mill, a pearl mill, the COBOL mill (all are trade names), etc. are mentioned.

[0055] Although technique, such as making size of the grinding media of a disperser small, enlarging the filling factor of grinding media and lengthening the processing time, making a regurgitation rate late, and classifying with a filter, a centrifugal separator, etc. after grinding, is used as an approach of obtaining the pigment which has desired particle size distribution in this invention, you may use combining such technique.

[0056] In addition, a pigment content and the pitch by which the pigment was adsorbed are settled using an ultracentrifuge etc. as an approach of measuring the amount (resin for which a pigment is not adsorbed) of the water soluble resin which is dissolving into the ink concerning this invention, and TOC (Total Organic Carbon, total-organic-carbon meter), a weight method (how to make carry out evaporation to dryness of the supernatant, and measure the amount of resin), etc. are suitably used in the amount of residual resin contained in this supernatant.

[0057] The ink of this invention is drainage system ink, and it is desirable that they are 50% or more of all ink weight as a content of water.

[0058] The ink jet record approach of having used the ink of this invention It is the ink jet record approach which gives the ink more than Isshiki from the recording head equipped with two or more ink deliveries at least to a recorded material without ink absorptivity, and forms a record image. The first process which carries out defecation processing of said recorded material front face, and the 2nd process which an ink droplet is made to fly according to an image recording signal, gives an ink droplet to the predetermined location of said recorded material, and forms a record image from the delivery of said recording head, The 3rd process which stiffens the ink given on said recorded material is included.

[0059] Furthermore, by the ink jet record approach of this invention, the 2nd process is preferably performed by the bubble jet recording method which makes an ink droplet breathe out according to an operation of heat energy.

[0060] On the other hand, the ink jet equipment which can be used for the ink jet record approach of this invention It is the ink jet recording device which gives the ink more than Isshiki from the recording head equipped with two or more ink deliveries at least to a recorded material without ink absorptivity, and forms a record image. a) The means which carries out defecation processing of said recorded material front face, the recording head equipped with two or more ink deliveries which an ink droplet is made to fly according to b image recording signal, and give an ink droplet to the predetermined location on said front face of a recorded material, and a means to stiffen the ink droplet of the c aforementioned image formation are provided.

[0061] In the equipment concerning this invention, the means of a may be omitted with a recorded material. Moreover, as technique, it is UV/O3. Washing is mentioned.

[0062] In the means of c), a (ultraviolet-rays UV) exposure lamp, an electron ray, heat, etc. are mentioned. In a UV irradiation lamp, since heat may occur and a recorded material may deform, when a cooler style, for example, a cold mirror, a cold filter, work-piece cooling, etc. possess, it is desirable.

[0063] Next, one example of the recording device which can be used for the ink jet record approach of above-mentioned this invention is explained.

[0064] Drawing 3 is the typical schematic diagram showing the whole recording device. Among drawing, 710 are a recording head and are the ink jet recording head of 360dpi64 nozzle. Furthermore, four heads for four classification by color of Y (yellow), M (Magenta), C (cyanogen), and Bk (black) are prepared, and it is set so that a full color image can be recorded by one scan. 701 is a recorded material. Two or more sheet recorded material 701 is set to the stocker 711, and it is sent to a band conveyor by the conveyance machine 712, and is sent out to the tray 715 for printing. 714 is an auxiliary roller for delivery.

[0065] Adsorption immobilization of the recorded material 701 sent to the tray 715 for printing is firmly carried out by suction with a pump 716 on a tray. The recorded material 701 on 715 is sent into the field to which the 1st down stream processing is performed. 704 is UV/O3. It is a lamp. With a recorded material, when surface NURE nature is low, this surface treatment is performed and the NURE nature of ink and adhesion are raised. This down stream processing may pass.

[0066] Shortly after a recorded material is taken out from the field of the 1st process by the delivery motor of 717, ink jet record by the recording head 710 is performed. Although a piezo method and various ink jet recording methods, such as an

electrostatic method, can be used for ink jet record which is this 2nd process, the Bubble Jet which is stabilized and can perform high-speed record is suitable.

[0067] Moreover, if it seems that problems, such as NIJIMI, occur as the record approach in one-pass printing, a two pass and 4 pass printing will be adopted.

[0068] The recorded material with which the image was recorded is immediately conveyed to the field to which processing of the 3rd process is performed. Here, 705 is a UV irradiation lamp.

[0069] Since heat occurs and deformation of a recorded material may be caused by the exposure of UV lamp, heating prevention devices, such as a cold mirror, a cold filter, and work-piece air cooling (un-[in a Fig.] illustrating above), are required.

[0070] The recorded material (record object which has a record image) which passed through the above three down stream processing is conveyed by the stocker 719 through a band conveyor 720 and the delivery roller 721, and is contained by the predetermined location with a handler 718.

[0071] In the illustrated example, although a recorded material 701 is the thing of a tabular configuration, the tray which conveys this is suitably adjusted so that it can respond to the configuration of a recorded material. For example, correspondence also in record to a disc-like recorded material is attained by using spacer 811 grade as shown in drawing 5. Moreover, as for this equipment, it is desirable to have a means to adjust the distance of a recording head and the image formation side of a recorded material according to the thickness of a recorded material.

[0072] Moreover, in order to promote the heat hardening in the 1st process and 3rd process, by forming heating means, such as a heater, in a tray auxiliary, for example, heating a recorded material before each processing, heating effectiveness is raised even to processing of a comparatively large-sized recorded material with big heat capacity, and effective processing is attained.

[0073] In addition, when it heat-treats, and deviation arises in a dimension, a gap of the cross direction of record and a feed direction arises and problems, such as generating of the white stripe in a record image and gap of printing size, arise by thermal expansion, as shown in drawing 6. It compares with the value beforehand set up with the comparator after detecting the skin temperature of the image formation side of a recorded material 901 with the thermo sensor 902, amplifying with the amplifier (Amp) and digitizing this by the A/D converter (A/D). It is desirable to use the system which adjusts a signal to a recording head 910 and a motor 903 by the optimal delay signal over the signal of a clock so that a recorded material can be set at delivery and a right location.

[0074] Moreover, in order to make a recorded material convey with a sufficient precision, marking of the mark can be carried out to the non-printing area of a recorded material with etching or a press, the location can be read with a suitable read means, the location of a recorded material can always be checked, a conveyance means can be controlled by the location, and more accurate conveyance can also be performed. Moreover, when a camber etc. is in a recorded material, it is also effective in a roller etc. to add the function which corrects a camber because of [, such as a camber,] amendment. Moreover, what is necessary is just to remove this with the means of a shirring press etc. after printing, if the aforementioned mark spoils product value.

[0075] Drawing 4 is the typical schematic diagram showing other whole recording device. 730 in drawing is for example, 360dpi at a recording head. It is the ink jet recording head of 64 nozzles. 730 is a head on which 730Y, 730M, 730C, and 730B print one color each of Y (yellow), M (Magenta), C (cyanogen), and B (black).

[0076] After printing yellow by 730Y, UV lamp of 705 performs UV irradiation and only UV which the front face of ink hardens at least is irradiated.

[0077] by the delivery motor of 717, the recorded material 701 on the conveyance tray 715 is conveyed to the place of the following 730M ink jet recording head in order to print the following color. An ink front face is stiffened with the 705UV lamp after printing. Then, a full color image is repeatedly formed with 730C and 730B. In addition, detail explanation is the same as explanation of drawing 3.

[0078] Although drawing 3 and drawing 4 are performing UV irradiation after one color or 4 color printing, a spot UV lamp may be installed beside an ink cartridge, and UV irradiation may be carried out for every one pass (un-illustrating).

[0079]

[Example] Next, an example explains this invention in more detail.

[0080] The ink of a presentation (weight ratio) as shown in one or less example was created. In addition, four colors of pigments were created.

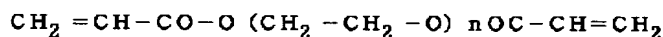
[0081]

[Table 1]

表 1

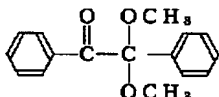
紫外線重合モノマー	* 1	7. 4 %
光開始剤	* 2	0. 4 %
水性顔料分散体	* 3	73. 8 %
(顔料/水溶性樹脂/水)		
界面活性剤	* 4	7. 4 %
水溶性溶剤	* 5	11. 1 %

* 1 : NKエステルA-400 (新中村科学)



(n = 9)

* 2 : イルガキュア651 (チバガイギー)



* 3 : シアン (顔料固形分16%)

マゼンタ (顔料固形分16%)

イエロー (顔料固形分16%)

ブラック (顔料固形分16%)

* 4 : ノイゲンET150、10% a q (第一工業製薬(株)製)

* 5 : イソプロピルアルコール (IPA) / ジエチレングリコール (DEG)

[0082] According to the flow of drawing 1, ink was created using the ink of the above-mentioned presentation, and the image was formed on the acrylic and the polycarbonate.

[0083] First, NK ester A-400 It is the IRUGA cure 651 to 2g. 0.1g was added and stirring was performed for about 10 minutes. Furthermore, IPA was added, it carried out for stirring 5 minutes, and viscosity was adjusted to 5cp (it considers as Solution A).

[0084] Next, 2g (10%aq) of noy genes was added to pigment ink (pigment / water-soluble-resin / water) 20g, and stirring was performed for about 30 minutes (it considers as Solution B). Pigment ink is beforehand adjusted to 5cp.

[0085] Pigment ink: Solution A and Solution B were mixed so that it might be set to monomer = 10:1, and the line was taken as ultraviolet curing ink for stirring 30 minutes. It is in the inclination for the glossiness of a printing hardened material to fall at the same time a regurgitation property will fall, if the amount of monomer increases about this compounding ratio.

[0086] First, the yellow ink of this above-mentioned constituent was used. After printing and printing with an ink jet printer as shows yellow ink to drawing 2, ultraviolet rays were irradiated at the printing section. the UV irradiation reinforcement at this time — 10 J/cm² it was. It hardened to the degree of hardness as which yellow ink is touched by the fingertip at this time, and a degree of hardness is sensed enough.

[0087] Next, it printed so that Magenta ink with the above-mentioned presentation might be lapped with the printing section of yellow ink in part. The ultraviolet rays after printing were irradiated and hardening of Magenta ink was checked.

[0088] In this example, the acrylic and the polycarbonate were used as a recorded material.

[0089] Although the part with which ink laps with an optical microscope was observed, there was no trace which has generated the blot and printing grace was good. Moreover, in the fitness of adhesion with a recorded material, even if rubbed, it did not peel.

[0090] Furthermore, also fading [of the color by UV irradiation] was not observed.

[0091] in this example, scratch nature improved the SN leveler H907 (Sannopuko) by [0.5% of] coming out comparatively and adding to the monomer in the ink of the above-mentioned presentation.

[0092] Furthermore, by carrying out little addition of the CHIEGU recall as an additive, fixing of a nozzle could be prevented and the printing engine performance improved.

[0093] Although UV irradiation irradiated after each color printing (10 J/cm²), since it stiffened the front face even if it printed the following color, since it stiffened each color completely, even if it printed the following color, it did not bleed, and formation of a good color picture was possible for it.

[0094] The ink of a presentation (weight ratio) as shown in the example 2 following was created. In addition, pigment ink is **** for 4 colors.

[0095]

[Table 2]

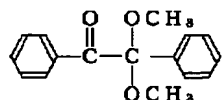
表2

紫外線重合モノマー	* 1	7.4 %
光開始剤	* 2	0.4 %
水性顔料分散体	* 3	73.8 %
(顔料/水溶性樹脂/水)		
界面活性剤	* 4	7.4 %
IPA		6.7 %
水		4.4 %

* 1 : LR8765 (BASF)

1. 4 ブタジオールのジエポキシアクリル酸エステル

* 2 : イルガキュア 651 (チバガイギー)



* 3 : シアン	(顔料固形分 16 %)
マゼンタ	(顔料固形分 16 %)
イエロー	(顔料固形分 16 %)
ブラック	(顔料固形分 16 %)

* 4 : ノイゲン 10 % aq

[0096] The manufacture approach of ink and the printing approach are the same as that of an example 1. Printing grace was good although printed on the acrylic and the polycarbonate. Moreover, adhesion with a recorded material was also good, and it also received rubbing and did not peel.

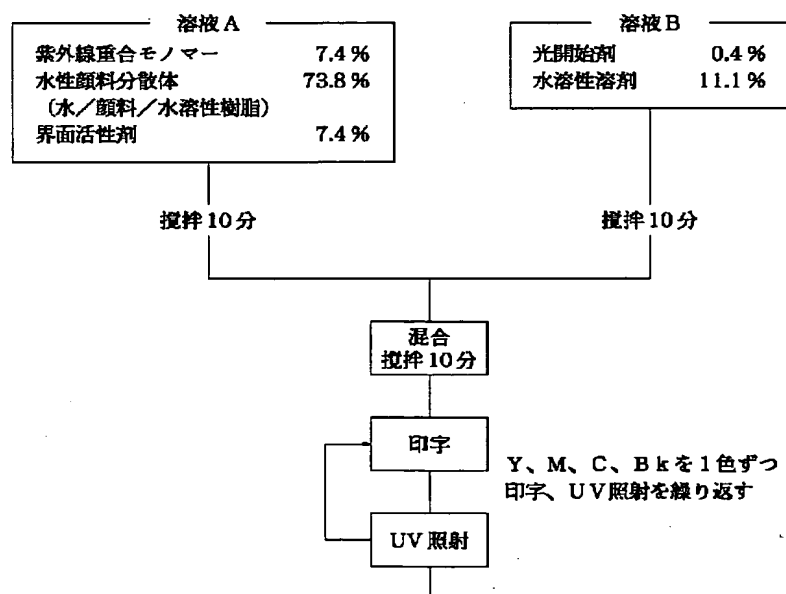
[0097] It created by the flow which shows the ink of a presentation as shown in the example 3 following below.

[0098] The used matter name is the same as a thing given in an example 1.

[0099]

[Table 3]

表3



[0100] Ink shelf life was good, without causing gelation by the dark reaction by keeping the ultraviolet-rays polymerization monomer and the photoinitiator separately.

[0101] The ink of a presentation (weight ratio) as shown in example 4 table 4 was created. First, the ultraviolet curing monomer and the weight ratio of a photopolymerization initiator were set to 1:0.05, and stirring was performed for about 10 minutes, and further, IPA of one 1.5 times the weight of this was added to monomer weight, it stirred for 5 minutes, and viscosity was adjusted to 5cps (it considers as Solution A).

[0102] Next, pigment ink (pigment / water-soluble-resin / water):color ink (a color/water) = it mixes so that it may be set to 10:0, 8:2, 5:5, 2:8, and 0:10 (it considers as Solution B).

[0103] Solution B: Solution A and Solution B were mixed, stirring was performed for 30 minutes, and it considered as ultraviolet curing ink so that it might be set to monomer = 10:1. Since the inclination for the feeling of gloss of a printing

hardened material to fall was suited while the regurgitation property fell when the amount of monomer increased about this compounding ratio, it was referred to as solution B:monomer =10:1.

[0104] After printing and printing a pigment and a color with an ink jet printer using four colors, respectively, they irradiated ultraviolet rays at the printing section. The UV irradiation reinforcement at this time, and OD value after an exposure and the viscosity of ink are doubled, and it lists to Table 4.

[0105]

[Table 4]

表4

*1 紫外線硬化 モノマー (%)	*2 顔料インク 10%溶液 (%)	*3 染料インク 10%溶液 (%)	*4 光重合開始 剤 (%)	IPA (%)	インク 粘度 (cp)	紫外線 強度 (J/cm ²)	OD	耐光性
8.0	79.7	—	0.4	12.0	7.3	10	○	○
8.0	63.7	15.9	0.4	12.0	6.5	5	○	○
8.0	39.8	39.8	0.4	12.0	4.1	2	○	○
8.0	15.9	63.7	0.4	12.0	3.4	0.3	△	△
8.0	—	79.7	0.4	12.0	3.0	0.1	△	×

*1: NK ester A-400 (new Nakamura chemistry)

$\text{CH}_2=\text{CH}-\text{CO}-\text{O}(\text{CH}_2-\text{CH}_2-\text{O})_n\text{OC}-\text{CH}=\text{CH}_2(n=9)$

*2: Cyanogen (10% of pigment solid content)

Magenta (10% of pigment solid content)

Yellow (10% of pigment solid content)

Black (10% of pigment solid content)

*3: Cyanogen — Pro jet cyanogen (10% of color solid content)

Magenta — Acid red (10% of color solid content)

Yellow — Direct yellow (10% of color solid content)

Black — Hood black (10% of color solid content)

*4: IRUGA cure 651 (Ciba-Geigy)

[0106] Although the setting time of ink became quick as the rate of a color increased, in connection with it, it fell, lightfastness also fell and OD value was performed. Therefore, it became clear as a ratio of a pigment and a color that 8:2-2:8 were suitable by the weight ratio.

[0107] In addition, the following approaches and criteria estimated the term of OD of front Naka, and the light-fast term.

[0108] [The approach of a radiationproofing test and valuation basis] Each ink of an example was printed to the 2cmx2cm solid pattern, the ultraviolet rays of the amount shown in front Naka were irradiated, and it was made to harden on a transparent polycarbonate resin plate. The test piece of the hardened solid pattern was attached in 0 m of atlas xenon fade, the continuous irradiation trial of 100 hours was performed, the reflection density of order was measured, and the OD rate of change R was calculated. Here, it is $R = [\text{OD before OD/exposure after exposure}] \times 100$. A valuation basis is $0:R \geq 900:90 > R \geq 80$ **: $80 \geq R > 60$ x: $60 > R$. It indicated by carrying out.

[0109] [Valuation basis of OD] The following criteria indicated OD.

0 : $\text{OD} \geq 1.20$: $1.2 > \text{OD} \geq 1.1$ **: $1.1 > \text{OD}$ [0110] Based on example 5 example 4, in order to investigate the optimal range further, the ratio of a pigment and a color was mixed so that it might be set to 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, and 2:8, and each property was investigated.

[0111] The result was listed to Table 5 (about an ingredient, it is the same as an example 4).

[0112]

[Table 5]

表5

紫外線硬化 モノマー (%)	顔料インク 10%溶液 (%)	染料インク 10%溶液 (%)	光重合開始 剤 (%)	IPA (%)	インク 粘度 (cp)	紫外線 強度 (J/cm ²)	OD	耐光性
8.0	63.7	15.9	0.4	12.0	6.5	5	◎	◎
8.0	55.7	23.9	0.4	12.0	5.5	3.8	◎	◎
8.0	47.8	31.8	0.4	12.0	4.7	2.7	○	○
8.0	39.8	39.8	0.4	12.0	4.1	2	○	○
8.0	31.8	47.8	0.4	12.0	3.7	1	○	○
8.0	23.9	55.7	0.4	12.0	3.5	0.5	○	○
8.0	15.9	63.7	0.4	12.0	3.4	0.3	△	△

From a cure rate and relation, such as lightfastness, the range of the ratios 7:3-3:7 of a pigment and a color is preferably suitable.

[0113] LR8765 (BASF) of the diepoxy acrylic ester of 1,4 Buta Diol was used for the example 6 ultraviolet-rays polymerization monomer, and ink was created with the same compounding ratio as examples 4 and 5.

[0114] Although the setting time of ink became quick as the rate of a color increased also in this case, in connection with it, OD value fell, lightfastness also fell and the same result as examples 4 and 5 was obtained.

[0115]

[Effect of the Invention] The following effectiveness has been checked the ink jet, especially the bubble jet recording head by the ink and the ink jet record approach by this invention as explained above.

[0116] ** Image formation becomes possible on a recorded material without ink absorptivity.

[0117] ** Since the blot between ink does not take place, formation of a color picture with good printing grace is attained.

[0118] ** The printing object in which a water resisting property and lightfastness are very excellent is obtained.

[0119] ** Ink with sufficient ink shelf life is obtained.

[0120] ** Since it is a drainage system, it is advantageous to an environment.

[Translation done.]

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(54) 発明の名称 インク、及びこれを用いるインクジェット記録方法と機器

(57) 要約

【目的】 被記録材、特に、インク吸収性のない被記録材に対して良好な記録が可能なインク、及びこれを用いるインクジェット記録方法と機器を提供する。

【構成】 水性液媒体中に、少なくとも顔料、水性性樹脂、エネルギーの付与により固体化する水性性モノマー、及び光重合開始剤を含むことを特徴とするインクである。更には、前記インクを用いたインクジェット記録方法、及びインクジェット用機器類である。

【特許請求の範囲】

【請求項1】 水性液媒体中に、少なくとも顔料、水性性樹脂、エネルギーの付与により固体化する水性性モノマー、及び光重合開始剤を含むことを特徴とするインク。

【請求項2】 前記水性性樹脂の重量平均分子量が3000乃至300000の範囲にある請求項1に記載のインク。

【請求項3】 前記顔料が分散状態にある請求項1に記載のインク。

【請求項4】 更に、染料を含む請求項1に記載のインク。

【請求項5】 前記顔料と前記染料とが、重量比で8:2〜2:8の範囲にある請求項4に記載のインク。

【請求項6】 前記水性性モノマーとして、多官能基を有するモノマーを含む請求項1に記載のインク。

【請求項7】 前記水性性モノマーを、インク全重量の1%〜10%の範囲で含む請求項1に記載のインク。

【請求項8】 前記エネルギーが、紫外線、熱又は電子線である請求項1に記載のインク。

【請求項9】 粘度を10c p s以下に調整した請求項1に記載のインク。

【請求項10】 pHを7〜10.0の範囲に調整した請求項1に記載のインク。

【請求項11】 インク全重量の50%以上の水を含む請求項1に記載のインク。

【請求項12】 インクジェット方式により形成したインク滴を被記録材に付着させて記録を行うインクジェット記録方法において、前記インクとして前記請求項1乃至11の何れか1に記載のインクを適用することを特徴とするインクジェット記録方法。

【請求項13】 前記インクジェット方式が、インクに熱エネルギーを用いる方式である請求項12に記載のインクジェット記録方法。

【請求項14】 前記被記録材がインク吸収性のないものである請求項12に記載のインクジェット記録方法。

【請求項15】 更に、被記録材に付着したインクに対し、紫外線、熱又は電子線を付与する過程を有する請求項12に記載のインクジェット記録方法。

【請求項16】 インクを収容したインク収容部を有するインクカートリッジにおいて、前記インクとして前記請求項1乃至11の何れか1に記載のインクを適用したことを特徴とするインクカートリッジ。

【請求項17】 インクを収容したインク収容部と前記インクをインク滴として吐出するためのヘッド部とを共に有する記録ユニットにおいて、前記インクとして前記請求項1乃至11の何れか1に記載のインクを適用したことを特徴とする記録ユニット。

【請求項18】 前記ヘッド部において、前記インクに熱エネルギーを用いるインク吐出を行う請求項17

に記載の記録ユニット。

【請求項19】 インクジェット方式により形成したインク滴を被記録材に付着させて記録を行うインクジェット記録装置において、前記請求項16乃至18の何れかに記載のインクカートリッジ又は記録ユニットを有することを特徴とするインクジェット記録装置。

【請求項20】 前記被記録材に対し、紫外線、熱又は電子線を照射する手段を、更に備えた請求項19に記載のインクジェット記録装置。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、インク、とりわけインク吸収性のない媒体への記録に適合するインクに関し、更には、このインクを用いるインクジェット記録方法、及びかかるインクを適用したインクジェット用機器類に関する。

【0002】

【従来の技術】 液体インクをヘッドノズルから噴射することにより印字するインクジェット記録装置のインクとしては、水系溶媒に色材として染料を溶解した水系インクと、常温で固化するワックス系溶剤に染料を溶解し、加熱溶解した状態でヘッドより噴射し印字するソリッドインクとがある。

【0003】 また、紫外線硬化型のインクジェットプリント用インクに関しては、特開平5-186725号公報に記載されている様に水性性染料を使用したものがあり、普通紙・再生紙への印字を容易にしたものである。

【0004】 また、ワックスチック基液・顔液形成方法としては、特開昭52-142516号公報に記載されているように紫外線硬化型樹脂に昇華性染料を用いている。

【0005】

【発明が解決しようとする課題】 従来の技術において、以下に示す問題がある。

【0006】 1、水系インクをカラー印字に用いる場合、例えば、第一色目に印字し、第一色目が乾燥した後、第二色目を印字する場合、第一色目に第二色目のドットが重なる点と、第一色目の染料が再溶解してびんてしまひ印字品位が悪化する問題があった。

【0007】 2、また、水系インクは紙への溶剤浸透性を利用して印字するため、被記録材としてプラスチックを用いるとインク乾燥までに時間がかかると同時に耐摩耗性のある画像を形成することができない。したがって、被記録材としては、紙が対象になってしまふ。

【0008】 3、紫外線硬化型樹脂に水性性染料を混合したインクでは、印字後再度水分が付着しても染料がにじむことはないが、紫外線照射による染料の退色は避けられない。

【0009】 4、ソリッドインクでは被記録材は選ばないが、ワックスという柔らかい材質であるために強い摩

【00033】本発明のインクにおいて好適な水性媒体は、水及び水溶性有機溶剤の混合溶液であり、水は顔々のイオンを含有する一般の水ではなく、イオン交換水（脱イオン水）を使用するのが好ましい。

【00034】水と混合して使用される水溶性有機溶剤としては、例えば、メチルアルコール、エチルアルコール、n-プロピルアルコール、イソプロピルアルコール、n-ブチルアルコール、sec-ブチルアルコール、tert-ブチルアルコール、イソ-ブチルアルコール等の炭化数1～4のアルキルアルコール類；ジメチルホルムアミド、ジメチルアセトアミド等のアミド類；アセトン、ジメチルソルコール類のケトアルコール類；テトラヒドロフラン、ジオキサン等のエーテル類；ポリエチレングリコール、ポリプロピレングリコール等のポリアルコレングリコール類；エチレングリコール、プロピレングリコール、グチレングリコール、トリエチレングリコール、1, 2, 6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコール等のアルキレン基が2～6個の炭素原子を含むアルキレングリコール類；グリセリン；エチレングリコールモノメチル（またはエチル）エーテル、ジエチレングリコールモノメチル（またはエチル）エーテル等の多価アルコールの低級アルキルエーテル類；N-メチル-2-ピロリドン、1, 3-ジメチル-2-イミダゾリジン等が挙げられる。

【00035】また、これらの多くの水溶性有機溶剤の中で、有機アミンは分散剤を中和し、インクのpHを中性～塩基性の領域に調節するために本発明のインク中に、好ましくはインク全体の0.001～10重量%含有させる。

【00036】また、有機アミン以外の上記水溶性有機溶剤については、所望に応じて適宜選択され、適量が含まれるが、中でもジエチレングリコール等の多価アルコール、トリエチレングリコールモノメチル（又はエチル）エーテル等の多価アルコールの低級アルキルエーテルが好ましい。

【00037】更に、吐出の安定性を得るためには、脂肪族一面アルコール、例えば、エタノール或はイソプロピルアルコールを3%以上添加することが効果的であることを見出した。即ち、これら溶剤を添加することによって、インクの液滴の発熱抵抗体上での発泡をより安定に行うことができるからと考えられる。

【00038】更に、これらの溶剤の効果としては、分散液にこれら溶剤を添加することにより、分散時における泡の発生が抑えられ、効果的な分散が行えることを挙げることができる。

【00039】また、本発明のインクは、上記の成分のほか、必要に応じて所望の物性を有するインクとすること、界面活性剤、消泡剤、防腐剤等を更に添加すること

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とができる。更に、市販の水溶性染料等も添加することができる。

【00040】例えば、界面活性剤としては、脂肪醇塩類、高級アルコール硫酸エステル塩類、液体脂肪油硫酸エステル塩類、アルキルアリルアルコール燐酸塩等の陰イオン界面活性剤、ポリオキシエチレンアルキルエーテル類、ポリオキシエチレンアルキルエステル類、ポリオキシエチレンソルビトールアルキルエステル類等の非イオン界面活性剤があり、これらの1種または2種以上を適宜選択して使用することができる。その使用量は分散剤により異なるが、インク全量に対して0.01～5重量%が望ましい。

【00041】この際、インクの表面張力は30dyne/cm以上になるように界面活性剤の添加量を決定することが好ましい。なぜなら、インクの表面張力がこれより小さい値を示すことは、本発明のような記載方式においては、ノズル先端の濡れによる印字よれ（インク滴の着弾点のズレ）等の好ましくない事態を引き起こすからである。

【00042】一般にインクジェット用インクに要求される性能としては、インクの粘度、表面張力及びpH等の物性が挙げられるが、水性顔料インクの様な分散系では、これらの物性を満足していてもインクの発泡が不安定である場合が多くあった。

【00043】そこで本発明若しくは、水性顔料インクで熱的に安定で、更に最適な発泡が可能なインクの性能を鋭意研究した結果、インク中に溶解している水溶性樹脂の量をインク全重量の2%以下、好ましくは1%以下とすること、抵抗体上においてインクが個々の運動条件でも正確に発泡し、更に長期にわたっても薄膜抵抗体上に堆積物を発生しないことを見出した。つまり、顔料に対して多量に余剰の水溶性樹脂がインク中に存在すると、薄膜抵抗体上において所定の熱エネルギーを与えても、インクが発泡しなかったリパルス印加の際により、これらの余剰の水溶性樹脂が不溶物となり薄膜抵抗体上に堆積してしまい、不吐出や印字の乱れを引き起こす原因となっていた。

【00044】ここで溶解している水溶性樹脂とは、インク中において顔料に吸着していない媒体中に溶解した状態の樹脂を指す。かかる溶解している水溶性樹脂の量を減らす1つの手段が、インク作成時に顔料と水溶性樹脂の比率を重量比で3:1～30:1、好ましくは10:3～30:1の範囲に調整することである。

【00045】更に、分散液中の顔料と水溶性樹脂の総量は、重量基準で10%以下、好ましくは3%以下であることが好ましい。その理由としては、分散液中に一定濃度以上の顔料と水溶性樹脂が存在しないと、分散を効率的に行い最適な分散状態を得ることができないからである。

【00046】本発明の水溶性顔料分散体の調製方法とし

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ては、はじめに、水溶性樹脂（分散樹脂）、アミン、水を少なくとも含有する水溶液に顔料を添加し、攪拌した後、後述の分散処理を用いて分散を行い、必要に応じて遠心分離処理を行い、所望の分散液を得る。次に、この分散液にポリメチルメタクリレートを含む上記で挙げた様な成分を加え、攪拌しインクとする。

【00047】ここで、本発明のインクとしては、好ましくはその粘度を10cps以下に調整される。

【00048】とりわけ、インク中に溶解している水溶性樹脂（顔料に未吸着の樹脂）の量を2%以下にするため

$$\text{アミンの量 (g)} = \frac{\text{樹脂の吸着アミンの分子数} \times \text{樹脂量 (g)}}{56000}$$

【00051】更に、顔料を含む水溶液を分散処理する前に、プレミキソングを30分間以上行うこともまた必要である。このプレミキソング操作は、顔料表面の濡れ性を改善し、顔料表面への吸着を促進するためのものである。

【00052】分散液に添加されるアミン類としては、モノエタノールアミン、ジエタノールアミン、トリエタノールアミン、アミノメチルプロパノール、アゼモア等の有機アミンが好ましい。

【00053】一方、本発明に使用する分散機は、一般に使用される分散機であれば、如何なるものでも良いが、例えば、ボールミル、ローミル、サンボミル等が挙げられる。

【00054】その中でも、高速型のサンボミルが好ましく、例えば、スーパーミル、サンボライオンダー、ピーズミル、アジタータミル、タレンミル、ダイノミル、ハールミル、コボルミル（いずれも商品名）等が挙げられる。

【00055】本発明において、所望の粒度分布を有する顔料を得る方法として、分散機の粉砕メダイアのサイスを小さくすること、粉砕メダイアの充填率を大きくすること、また処理時間を長くすること、吐出速度を遅くすること、粉砕後にフィルターや遠心分離機等で分散すること等の手法が用いられるが、これらの手法を組合わせて用いてもよい。

【00056】尚、本発明にかかるインク中に溶解している水溶性樹脂の量（顔料に未吸着の樹脂）を測定する方法としては、超遠心分離機等を用いて顔料分と顔料に吸着された樹脂分を分離させ、この上澄み液に含有される残存樹脂量をTOC (Total Organic Carbon, 全有機炭素量) や、重量法（上澄みを蒸発乾燥させ、樹脂量を測定する方法）等が好適に用いられる。

【00057】本発明のインクは水系インクであり、水の含有量としてはインク全重量の50%以上であることが好ましい。

【00058】本発明のインクを利用したインクジェット記録方法は、インク吸収性のない被記録材に対して、イ

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*には、作成方法において、樹脂、アミン及び水を含む水溶液を60℃、3分間以上攪拌して樹脂を予め完全に溶解させることが必要である。

【00049】また、樹脂を溶解させるアミンあるいは塩基の量を、樹脂の樹脂から計算によって求めたアミンあるいは塩基量の1.2倍以上添加することが必要である。このアミンあるいは塩基の量は以下の式によって求められる。

$$\text{アミン} \quad \text{【外1】} \quad \text{【00050】}$$

【00059】更に本発明のインクジェット記録方法では、好ましくは第2の工程は熱エネルギーの作用によりインク滴を吐出させるバブルジェット記録方式によって行われる。

【00060】一方、本発明のインクジェット記録方法に用い得るインクジェット装置は、インク吸収性のない被記録材に対して、インク吐出量を複数備えた記録ヘッドから少なくとも一色以上のインクを付与して記録画像を形成するインクジェット記録装置であって、

a) 前記被記録材表面を洗浄処理する手段と、

b) 画像記録信号に応じてインク滴を排出させ、前記被記録材表面の所定位置にインク滴を付与するインク吐出量を複数備えた記録ヘッドと、

c) 前記画像形成のインク滴を硬化させる手段とを具備する。

【00061】本発明に係る装置において、a) の手段は、被記録材によって省略してもかまわない。また手法としては、UV/O₃ 洗浄が挙げられる。

【00062】c) の手段において、紫外線 (UV) 照射ランプ、電子線、熱などから挙げられる。UV照射ランプにおいては、熱が発生し被記録材が変形してしまう可能性があるので、冷却機構、例えばコールドスロー、コーラドファンクター、クーラ冷却などが具備されていると好ましい。

【00063】次に、上記の本発明のインクジェット記録方法に用い得る記録装置の一例について説明する。

【00064】図3は、記録装置全体を示す模式的概略図である。図中、710は記録ヘッドで、360dpiの4ノズルのインクジェット記録ヘッドである。更に、Y (イエロー)、M (マゼンタ)、C (シアン)、Bk

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(ブラック)の4色分用の4つのヘッドが設けられ、一走査でフルカラーの画像を記録できるようにセットされている。701は被記録材である。ストッカー711に複数枚被記録材701がセットされており、搬送機712によりベルトコンベアーに送られ、印字用ロー715に送り出される。714は、送りのための補助ローである。

【0065】印字用ロー715に送られた被記録材701は、ホゾ716での吸引によりロー上につかりと吸着固定される。715上の被記録材701が第1の処理工程が行われる領域に送り込まれる。704はUV/O₃ランプである。被記録材により、表面のメレ性の低い場合は、この表面処理を行い、インクのスレ性、密着性を向上させる。この処理工程はバズしても構わない。

【0066】717の送りモータで第1の工程の領域から被記録材が搬出されると、直ちに記録ヘッド710によるインクジェット記録が行われる。この第2の工程であるインクジェット記録には、ピエゾ方式や、静電方式など種々のインクジェット記録方式が利用できるが、高速記録を安定して行うことのできるバブルジェット方式が好適である。

【0067】また、記録方法としては、1パス印字の場合にニジミなどの問題が発生するようであれば、2パス、4パス印字が採用される。

【0068】画像が記録された被記録材は、第3の工程の処理が行われる領域に直ちに搬送される。ここで、705はUV照射ランプである。

【0069】UVランプの照射によって熱が発生し、被記録材の変形を起こす可能性があるため、コールドミラー、コールドフイルター、ワーク空冷(以上図中不図示)等の加熱防止機構が必要である。

【0070】以上の3つの処理工程を経た被記録材(記録画像を有する記録物)は、ベルトコンベアー720と送りロー721を介してストッカー719に搬送され、ハンドラー718によって所定位置に収納される。

【0071】図示した例においては、被記録材701は板状形状のものであるが、これを搬送するローは被記録材の形状に対応できるように適宜調節される。例えば、図5に示すようなスプアー811等を用いることで円盤状の被記録材への記録にも対応可能となる。また、この装置は、被記録材の厚みに応じて記録ヘッドと被記録材の画像形成面との距離を調整する手段を有していることが望ましい。

【0072】また、第1の工程や第3の工程における加熱硬化を促進するためには、ローにヒーター等の加熱手段を補助的に設けて、例えば被記録材を各処理前に加熱しておくことで、熱容量の大きな比較的大型の被記録材の処理にでも加熱効率を高めて効果的な処理が可能となる。

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【0073】尚、加熱処理を行った際に、熱膨張によって寸法に狂いが生じ、記録の幅方向及び送り方向のずれが生じ、記録画像でのバズシの発生や印字サイズのズレ等の問題が生ずる場合には、例えば図6に示すように、被記録材901の画像形成面の表面温度を温度センサ902で検出し、増幅器(Amp)で増幅し、これをA/Dコンバータ(A/D)でデジタル化してからコンパレータで予め設定された値と比較して、クロックの信号に対する最速デジタル信号で記録ヘッド910とモータ903へ信号を送り、正しい位置に被記録材をセットできるように調整するシステムを用いるのが好ましい。

【0074】また、被記録材の位置を精度よく搬送するためには、被記録材の非印字領域にエッチングやメスによって目印をマーキングし、その位置を適当な読取り手段で読み取り、被記録材の位置を常に確認し、その位置によって搬送手段を制御してより精度よい搬送を行うこともできる。また、被記録材にソリ等がある場合には、ソリ等の補正のためにロー等にソリを矯正する機能を付加しておくことも有効である。また、前記の目印が製品価値を損なうものであれば、印字後にシャリソングラス等の手段によりこれを取り除けばよい。

【0075】図4は、他の記録装置全体を示す模式的概略図である。図中730は、記録ヘッドで例えば360dpi、64ノズルのインクジェット記録ヘッドである。730は730Y、730M、730C、730B、730BはY(イエロー)、M(マゼンタ)、C(シアン)、B(ブラック)の各1色を印字するヘッドである。

【0076】730Yでイエローを印字した後、705のUVランプによりUV照射を行い、少なくともインクの表面が硬化しただけのUVを照射する。

【0077】717の送りモータで、搬送ロー715上の被記録材701は次の色の印字を行うため、次の730Mインクジェット記録ヘッドのところへ搬送される。印字後705UVランプにより、インク表面を硬化させる。続いて730C、730Bと繰り返し送り、フルカラーの画像が形成される。その他詳細説明は図3の説明と同様である。

【0078】図3、図4は1色または4色印字後にUV照射を行っているが、インクカカリソリソリにスポットUVランプを設置し、1パス毎にUV照射してもかまわない(不図示)。

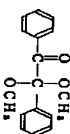
【0079】
【実施例】次に、本発明を実施例により更に詳しく説明する。

【0080】実施例1
以下に示すような組成(重量比)のインクを作成した。尚、顔料は4色作成した。

【0081】
【表1】

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成分	重量割合	単位
紫外線重合モノマー	*1	
光増感剤	*2	
水性顔料分散体	*3	
(顔料/水増感剤/水)		
界面活性剤	*4	
水増感剤	*5	
*1: NKエスエムA-400 (新中村化学)		
*2: CH ₂ =CH-CO-O (CH ₂ -CH ₂ -O) nOC-CH=CH ₂		
*3: 4-イソプロピル-1,5-ジエチル-2,6-ジメチル-4-ヒドロキシベンゼン		
*4: 4-イソプロピル-1,5-ジエチル-2,6-ジメチル-4-ヒドロキシベンゼン		
*5: 4-イソプロピル-1,5-ジエチル-2,6-ジメチル-4-ヒドロキシベンゼン		



*3: ソリ	(顔料顔料分10%)
マゼンタ	(顔料顔料分10%)
イエロー	(顔料顔料分10%)
ブラック	(顔料顔料分10%)
*4: 4-イソプロピル-1,5-ジエチル-2,6-ジメチル-4-ヒドロキシベンゼン	(第一工増感剤(水) 配)
*5: 4-イソプロピル-1,5-ジエチル-2,6-ジメチル-4-ヒドロキシベンゼン	(第二工増感剤(水) 配)

【0082】上記組成のインクを用いて図1のフローに従ってインクを作成し、アクリル、ポリカーボネート上に画像を形成した。

【0083】まず、NKエスエムA-400 2gにイソプロピルエーテル 0.1gを加え、約10分間攪拌を行った。更にIPAを追加し攪拌5分を行い、粘度を5cPに調整した(溶液Aとする)。顔料インクはあらかじめ5cPに調整してある。

【0084】次に顔料インク(顔料/水増感剤/水)20gにイソプロピルエーテル(10%aq)を2g添加し約30分攪拌を行った(溶液Bとする)。顔料インクはあらかじめ5cPに調整してある。

【0085】顔料インク:モノマー=10:1となるように溶液Aと溶液Bを混合し、攪拌30分行って紫外線硬化インクとした。この配合比に關してモノマー分が多くなると吐出特性が低下すると同時に印字硬化物の光沢度が低下する傾向にある。

【0086】まず、この上記組成物のイエローインクを用いた。イエローインクを図2に示すようなインクジェットプリンターで印字して、印字した後に印字部に紫外線を照射した。この時の紫外線照射強度は10J/cm²であった。この時点でイエローインクは指先でさわって十分硬さが感じられる硬さに硬化した。

【0087】次に、上記組成物を持つマゼンタインクをイエローインクの印字部に一部重なるように印字を行った。印字後紫外線を照射し、マゼンタインクの硬化を確認した。

【0088】本実施例において被記録材としてアクリル、ポリカーボネートを用いた。

【0089】光学顕微鏡でインクの重なる部分を観察し

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成分	重量割合	単位
紫外線重合モノマー	*1	
光増感剤	*2	
水性顔料分散体	*3	
(顔料/水増感剤/水)		
界面活性剤	*4	
水増感剤	*5	
*1: NKエスエムA-400 (新中村化学)		
*2: CH ₂ =CH-CO-O (CH ₂ -CH ₂ -O) nOC-CH=CH ₂		
*3: 4-イソプロピル-1,5-ジエチル-2,6-ジメチル-4-ヒドロキシベンゼン		
*4: 4-イソプロピル-1,5-ジエチル-2,6-ジメチル-4-ヒドロキシベンゼン		
*5: 4-イソプロピル-1,5-ジエチル-2,6-ジメチル-4-ヒドロキシベンゼン		

【0090】更に、紫外線照射による色の退色も観察された。

【0091】本実施例において、上記組成のインクにS N-ベンザル-H907 (サンゾコ) をモノマーに対して0.5%の割合で添加することにより熱過性は向上した。

【0092】更に添加剤としてチエグリニールを少量添加することにより、ノズルの閉塞が防止でき、印字性能は向上した。

【0093】紫外線照射は、各色印字後に照射(10J/cm²)を行ったが、各色とも完全に硬化させてから次の色を印字しても、表面を硬化させてから次の色を印字してもにじむことはなく、良好なカラー画像の形成が可能であった。

【0094】実施例2
下記に示すような組成(重量比)のインクを作成した。なお顔料インクは4色用いた。

【0095】
【表2】

【0096】
【表3】

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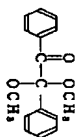
表2

紫外線硬化モノマー	*1	7.4%
光重合剤	*2	0.4%
水性顔料分散体	*3	73.8%
(顔料/水性樹脂/水)		
界面活性剤	*4	7.4%
IPA		8.7%
水		4.4%

*1: LR8765 (BASF)

*2: 4-ブチルフェニルジエチルアミンエスチル

*3: イルガキュア7851 (チバガイギー)



*3: シブソ

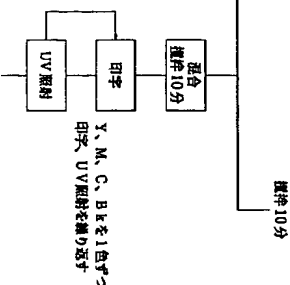
*4: ヲセツク

*4: ヲセツク

*4: ヲセツク

表3

溶液A	7.4%
紫外線硬化モノマー	73.8%
水性顔料分散体	7.4%
(水/顔料/水性樹脂)	
界面活性剤	
溶液B	0.4%
光重合剤	11.1%
水性樹脂	



【0100】紫外線硬化モノマーと光開始剤が別々に保管されていることにより、時反応によるゲル化を起こすこともなく、インク保存性が良好であった。

【0101】実施例4

表4に示すような組成(重量比)のインクを作成した。まず、紫外線硬化モノマーと、光重合開始剤の重量比を1:0.05とし、約10分間攪拌を行い、更にモノマー一重量に対し、1.5倍の重量のIPAを添加し、5分間攪拌し、粘度を5cpsに調整した(溶液Aとする)。

【0102】次に、顔料インク(顔料/水性樹脂/水):染料インク(染料/水)=10:0.8:2.

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【0096】インクの製造方法及び印字方法は、実施例1と同様である。アクリル、ポリカーボネイト上に印字してみたが、印字品位は良好であった。また、被印刷材との密着性も良好であり、こすりに対してははがれることもなかった。

【0097】実施例3

下記に示すような組成のインクを次に示すフローによって作成した。

【0098】使用した物質名は実施例1に記載のものと同一である。

【0099】

【表3】

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記する。

【0105】

*【表4】

表4

*1 紫外線硬化 モノマー (%)	*2 染料インク 10%溶液 (%)	*3 染料インク 10%溶液 (%)	*4 光重合開始 剤 (%)	IPA 含量 (%)	IPA 粘度 (cP)	紫外線 透過率 (%)	OD	耐光性
8.0	73.7	-	0.4	12.0	7.3	10	○	○
8.0	63.7	15.9	0.4	12.0	6.5	5	○	○
8.0	39.8	39.8	0.4	12.0	4.1	2	○	○
8.0	15.9	63.7	0.4	12.0	3.4	0.3	△	△
8.0	-	73.7	0.4	12.0	3.0	0.1	△	×

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*1: NKエスチルA-400 (新中村化学)

$$\text{CH}_2=\text{CH}-\text{CO}-\text{O}(\text{CH}_2-\text{CH}_2-\text{O})_n\text{OC}-\text{CH}=\text{CH}_2 \quad (n=9)$$

*2: シブソ (染料固形分10%)

*3: ヲセツク (染料固形分10%)

*4: イルガキュア7851 (チバガイギー)

*1: シブソ...アジソトリブソ (染料固形分10%)
*2: ヲセツク...アジソトリブソ (染料固形分10%)
*3: ヲセツク...アジソトリブソ (染料固形分10%)
*4: イルガキュア7851 (チバガイギー)

【0106】染料の割合が増すにつれて、インクの硬化時間が速くなるが、それとともないOD値は下がり、耐光性も低下して行った。よって、顔料と染料の比率として、重量比で8:2~2:8が適していることが判明した。

【0107】尚、表中のODの項、耐光性の項については、以下の方法及び基準により評価した。

【0108】(耐光性試験の方法及び評価基準) 透明なポリカーボネート樹脂板上に実施例の各インクを、2cm×2cmのベタパターンに印刷し、表中に示した量の紫外線を照射し、硬化させた。硬化したベタパターンの

試験片をアトラスキセノフエードOメーターに取り付け、10.0時間の連続照射試験を行い、前後の反射率を測定し、OD変化率Rを計算した。ここで、R=[照射後のOD/照射前のOD]×10.0である。評価基準は、

*1: R≥90

*2: 90>R≥80

*3: 80>R>60

*4: 60>Rとして記載した。

【0109】[ODの評価基準] ODは以下の基準で記載した。

*1: OD≥1.2

*2: 1.2>OD≥1.1

*3: 1.1>OD

*4: 1.0>OD

【0110】実施例5
実施例4に基づき、更に最速範囲を調べるために顔料と染料の比率を8:2、7:3、6:4、5:5、4:6、3:7、2:8になるように混合し、それぞれの特性を調べた。

【0111】結果を表5に列記した(材料については実施例4と同じである)。

【0112】

【表5】

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紫外線硬化モノマー		顔料イソソ 10%溶液	染料イソソ 10%溶液	光重合開始 剤	IR (%)	イソソ 純度 (%)	紫外線 強度 (J/cm ²)	OD	耐光性
8.0	63.7	15.9	0.4	12.0	6.5	5	③	③	
8.0	55.7	23.9	0.4	12.0	6.5	3.8	③	③	
8.0	47.8	31.9	0.4	12.0	4.7	2.7	○	○	
8.0	38.8	38.9	0.4	12.0	4.1	2	○	○	
8.0	31.8	47.8	0.4	12.0	3.7	1	○	○	
8.0	23.9	55.7	0.4	12.0	3.5	0.5	○	○	
8.0	15.9	63.7	0.4	12.0	3.4	0.3	△	△	

表5

硬化速度と耐光性などの関係から、好ましくは顔料と染料の比率7:3〜3:7の範囲が適している。

【0113】実施例6

紫外線重合モノマーに1,4-ブタジエールのジエポキシアクリル酸エステル（LR8765（BASF））を用いて、実施例4、5と同様の配合比でイソソを作成した。

【0114】この場合も、染料の割合が増すにつれて、イソソの硬化時間が速くなるが、それに伴いOD値は下がり耐光性も低下し、実施例4、5と同様の結果が得られた。

【0115】

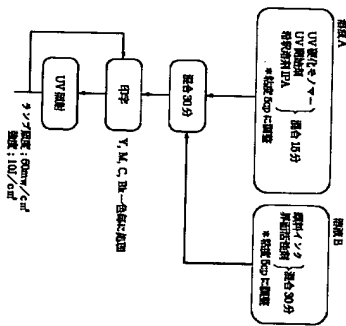
【発明の効果】以上説明したとおり、本発明によるイソソ及びイソソジェット記録方法により、イソソジェット特にバブルジェット記録ヘッドにより、次の効果が確認できた。

- 【0116】①イソソ吸収性のない被記録材上に画像形成が可能になる。
- 【0117】②イソソ間のにじみが起こらないため印字品位良好なカラー画像の形成が可能になる。
- 【0118】③耐水性、耐光性が非常に優れている印字物が得られる。
- 【0119】④イソソ保存性の良いイソソが得られる。
- 【0120】⑤本系であるため簡便に對して有利である。

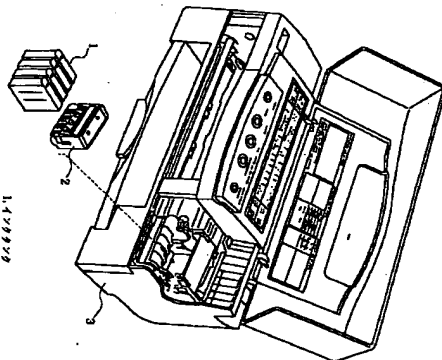
【図面の簡単な説明】

- 【図1】本発明によるイソソの1実施例のプロセスフローを示す図。
- 【図2】本発明によるイソソを使用した実施例のイソソ

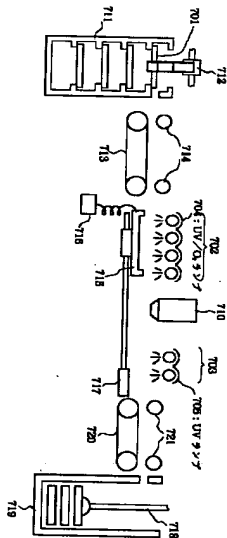
【図1】



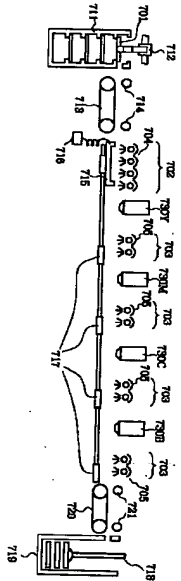
【図2】



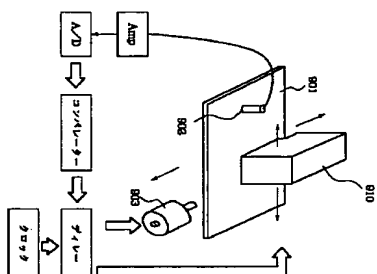
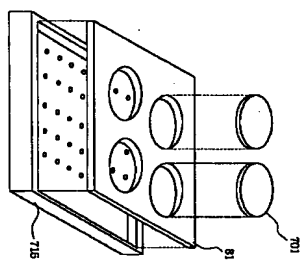
【図3】



【図4】



【图6】



フロントページの続き

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